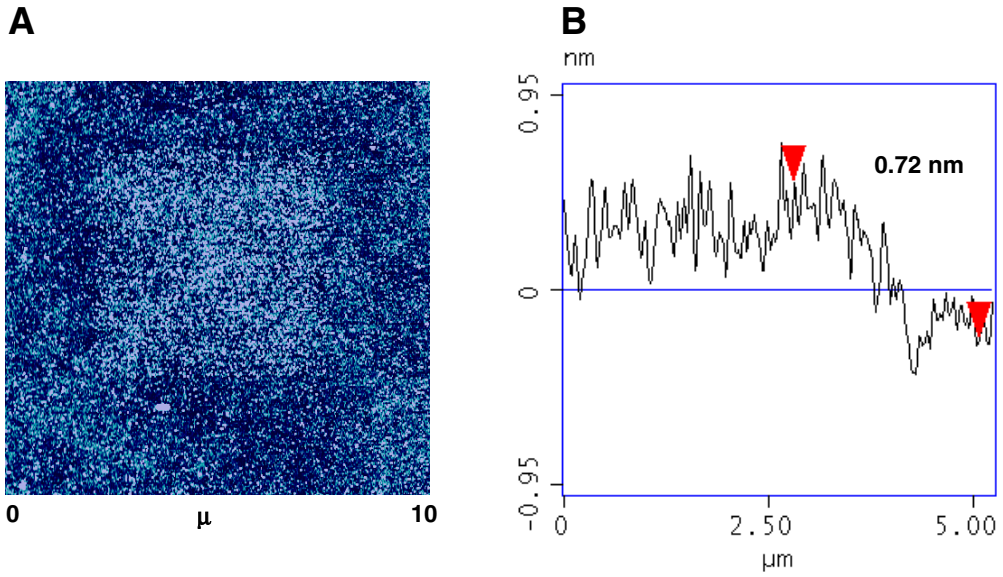
Dip-Pen Nanolithography of Reactive Alkoxysilanes on Glass

Hyungil Jung, Rajan Kulkarni, C. Patrick Collier

Supporting Information:

Estimation of MPTMS thickness from tapping mode imaging in water.

Figure 1. (A) AFM topography image of a 5 µm square pattern of 3'-mercaptopropyltrimethoxy-silane (MPTMS). The pattern was written at 0% relative humidity (RH) and then immediately transferred to the fluid cell for tapping mode imaging in water. Tapping mode AFM in air resulted in inverse height contrast due to the presence of residual water at the surface, even at 0% RH. This effect has been seen before with tapping mode AFM imaging of self-assembled monolayers.[1] (B) Average of cross-sectional traces of the height taken perpendicularly to the top edge of the pattern. The height difference between the two arrows is the reported thickness of a monolayer of MPTMS (7.2± 0.6 Å) measured with variable angle ellipsometry.[2]

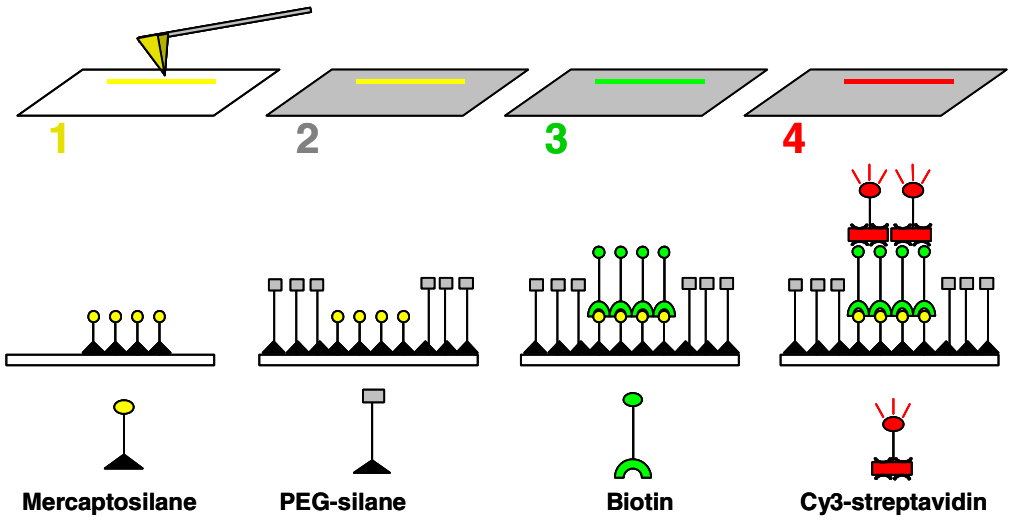


Biotin/streptavidin conjugation to MPTMS patterned areas:

Glass substrates (VWR #1 coverslips) were sonicated in piranha solution for one hour, and further cleaned in a 5:1:1 (v/v/v) mixture of H_2O, 30% H_2O_2 and 29% NH_4OH at 85° C for 10 minutes, followed by a 6:1:1 (v/v/v) mixture of H_2O, 30% H_2O_2 and concentrated HCl at 85° C for 10 minutes (*caution: these mixtures reacts violently with organic materials*). Millipore Gradient water was used throughout. Cleaned coverslips were stored in 25% ethanolic solution for up to two weeks. Coverslips were dried at 120° C before use.

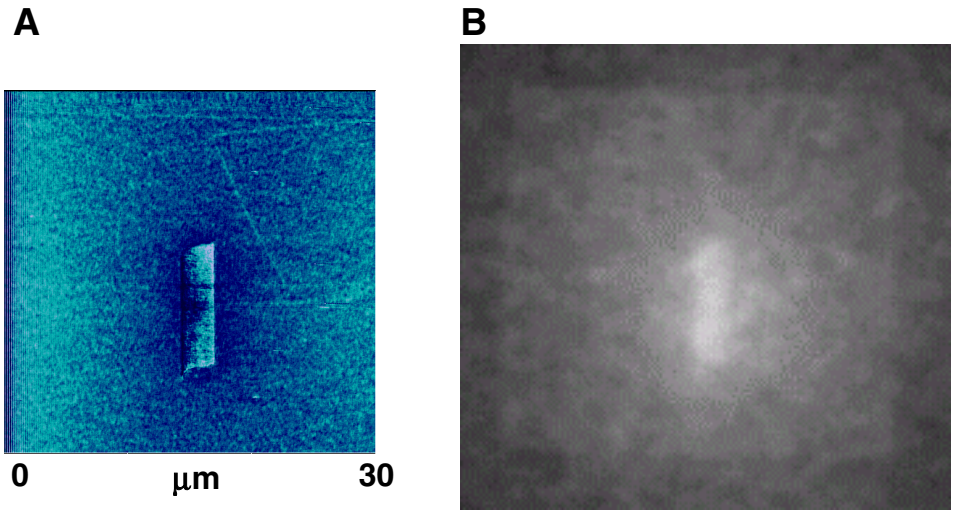
Unpatterned areas on glass were passivated against non-specific adsorption of proteins with a 3 mM solution of 2-[methoxy(polyethylenoxy)propyl]trimethoxysilane (PEG-silane, MW 460-590, Gelest) in toluene containing 0.8 mL/L concentrated HCl for 1 hour. After washing in toluene (once), ethanol (twice), and water (twice), the sample was soaked in 1 mL of 2 mM (+)-Biotinyl-3-maleimidopropionamidyl-3,6-dioxa-octanediamine (EZ-Link™ PEO-maleimide activated biotin, Pierce) in PBS buffer (pH 7.2) for 2 hours. The sample was incubated for 10 min using 2 μg/mL of Cy3-streptavidin in PBS buffer with 0.02% (v/v) Tween 20 detergent, and then washed several times in PBS buffer containing 0.1% Tween 20, rinsed with Millipore water and dried under N_2 gas.

Scheme 1.



MPTMS deposition during LFM imaging:

Figure 2. (A) LFM and (B) fluorescent images of the same MPTMS pattern. The LFM image shows a change in contrast from dark to bright indicative of polymerization-induced disorder during the course of DPN writing under ambient conditions. The corresponding fluorescent image after conjugation of the MPTMS pattern with biotin and Cy3-streptavidin shows that LFM scanning results in a faint fluorescent background. Apparently, MPTMS is deposited by the coated tip during LFM imaging, even at the fastest scan speeds used (183 μm/s).



References

[1] Neves, B.R.A.; Leonard, D.N.; Salmon, M.E.; Russell, P.E.; Troughton Jr., E.B. *Nanotechnology* **1999**, *10*, 399.
[2] Senkevich, J.J.; Mitchell, C.J.; Yang, G.-R.; Lu, T.-M. *Langmuir* **2002**, *18*, 1587.